ENVIRONMENTALLY FRIENDLY 'GREEN' PROPELLANT FOR THE MEDIUM CALIBER TRAINING ROUNDS

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ABSTRACT

U.S. Army TACOM-ARDEC has teamed with the U.S. Army Research Laboratory in developing an environmentally friendly 'green' propellant with improved insensitive munitions characteristics for use in medium caliber ammunition.

The propellant formulation, PAP8386, removes several toxins and carcinogens and is manufactured using a solventless process that eliminates volatile organic compounds. The material has been successfully processed by ATK under contract DAAE30-01-9-0800 TOSA 59/88 at the Radford Army Ammunition Plant on large-scale production equipment.

Preliminary tests have shown vastly improved hazard sensitivity and mechanical properties relative to existing fielded propellants in the Army inventory. Initial ballistic test results are very promising. Future work to optimize the geometry to improve the ballistic performance is planned.

1. INTRODUCTION

Executive Order 12856 of 3 August 1993, paragraph 3-303 requires each Federal Agency to establish a plan and goals for eliminating or reducing the unnecessary acquisition of products containing extremely hazardous substances or toxic chemicals. Furthermore, DODD 5000.1 paragraph 23 states that "All systems containing energetic material will comply with Insensitive Munitions criteria."

Barium nitrate (BaN), DiButyl phthalates (DBP), and diphenyl amine (DPA) are widely used in a multiplicity of propellants for medium caliber ammunition. Over the next five years an estimated 38,500 pounds of DPA, 44,000 pounds of DBP, and 10,000 pounds of BaN will be incorporated into medium caliber ammunition via the propellant. These materials are toxic, hazardous, or carcinogenic.

DBP, currently used as a plasticizer in several medium caliber propellant formulations, is a known carcinogen. Operators in the propellant manufacturing plant that are continuously exposed to DBP are more likely to develop liver, bile duct, and bladder cancers. DPA, which acts as a stabilizer against exothermic nitrocellulose degradation reactions in many propellant formulations, is a known toxin and contains a carcinogenic impurity (4-aminobiephenyl). This impurity can be absorbed into the body by inhalation of its aerosol, through the skin, and by ingestion. BaN is a moderately poisonous heavy metal compound that is often used as an oxidizing agent to enhance propellant ignition characteristics. It can irritate the mucous membranes and the skin producing dermatitis and eye, nose, and ear irritation.

The use of these materials in ammunition presents a hazardous environment for the propellant manufacturing operators and surrounding communities. Contamination of firing ranges by these ingredients jeopardizes sustained range use for training and could lead to very expensive cleanup needs. Finally, any eventual demilitarization or scrap disposal of aging rounds is complicated by the environmental hazards associated with the propellant ingredients.

In an effort to supply an environmentally friendly propellant for medium caliber ammunition applications that also improves the insensitive munitions characteristics, ARDEC directed ATK under contract DAAE30-01-9-0800 TOSA 59/88 to produce small

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quantities of a solventless propellant for the 25mm M793 round.

The M793 TP-T is a low cost target practice cartridge ballistically matched to the M792 HEI-T (High Explosive Incendiary with Tracer) and the MK210 HEI-T rounds. The cartridge can be fired from any platform that uses the M242 Bushmaster, KBA, M811 or GAU-12 weapons such as the Bradley Fighting Vehicle. It was chosen as a good candidate that would be representative of the 25mm ammunition family.

2. DEVELOPMENT APPROACH

2.1 Propellant Formulation and Processing

A number of formulations were considered for this project. To achieve the desired goals of meeting existing performance levels for the M793 round, eliminating environmental problems, and improving the insensitive munitions characteristics, a propellant manufactured using the solventless process was considered ideal.

The solventless propellant manufacturing process relies on energetic plasticizing agents such as nitroglycerine (NG) or diethylene glycol dinitrate (DEGDN) mixed with nitrocellulose to create the appropriate material properties that allow for extrusion of the propellant grains through a heated press. The plasticizers in the propellant formulation give the final product more ductile material properties relative to propellants that are manufactured using a solvent process. This ductility gives the material more desirable response to impact related IM threat scenarios such as bullet impact, fragment impact and shaped charge jet impact.

In the solvent process, ether and ethanol (volatile organic compounds, VOC) are typically used to give the nitrocellulose the proper consistency to be extruded. The solvents are then extracted from the propellant as part of the finishing process. The result is a more brittle propellant that tends to break up under impact. Another environmental concern associated with the solvent process is the inevitable loss to the atmosphere of the above mentioned VOC's.

Given the desire to use a solventless process, Cheetah 4 was used to investigate the thermochemistry of several potential candidates (Fried, 2005). The final formulation that was settled upon was given the identifier, PAP-8386. Cheetah 4 was used to determine the thermochemical constants needed for performance modeling and closed bomb burn rate determination. These values are shown in Table 1 for a loading density of 0.2 g/cc.

Table 1. Thermochemical results for PAP8386 from Cheetah 4 at a 0.2 g/cc loading density

Thermochemical Parameter	Value
Flame Temperature, [K]	2948
Impetus, [J/g]	1063.6
Gas Molecular Weight, [g/gmol]	23.049
Covolume, [cc/g]	1.042
Frozen Gamma	1.244

2.2 Preliminary Performance Assessment

The choice of a solventless process coupled with more environmentally friendly ingredients fulfilled one element of the overall design objectives. The remaining requirements were to meet performance and improve IM characteristics. An initial assessment of the PAP8386 in the M793 round was carried out using the CONPRESS model (Oberle, 1993). This model evaluates propellant performance purely from an energy level only. It applies the perfect interior ballistic cycle to the system and ignores any energy losses.

The CONPRESS model showed that PAP8386 could achieve the performance needs for the M793 if it were 88-90% efficient relative to the perfect ballistic cycle. Achieving this level of efficiency is not difficult. The performance requirements for the round are shown in Table 2.

Table 2. Performance specifications for the M793 cartridge.

Performance Measure	Value
Ambient Muzzle Velocity	1100 m/s
Max. Pressure (All Temps)	496 MPa
Max Amb. Pressure	402 MPa

The CONPRESS evaluation clearly showed the PAP8386 formulation to have sufficient chemical energy to meet the M793 performance needs. The next step required an appropriate grain design to effectively release the propellant's chemical energy and convert it to projectile kinetic energy. The Army Research Laboratory supported this effort by modeling the round using the ARL developed IBHVG2 (Interior Ballistics for High Velocity Guns) computer model (Anderson and Fickie, 1987).

This code is capable of evaluating, from an ideal perspective; the different propellant grain configurations and determining the optimum grain geometry to most

effectively meet the velocity and pressure requirements for the M793 round. From a processing standpoint, the small grain sizes needed for medium caliber ammunition and the available extrusion hardware limited the granulation choices to single perforated cylindrical grain or a cylindrical flake. The model results were run to determine the optimum length, outer diameter and inner diameter for the single perforated granular propellant.

From the available information on the propellant, which includes burn rates, chemical composition, and absolute density, the predicted web size (burn distance between the outer and inner diameters) for the M793 is 0.61 mm (0.024"). To ensure ballistic success, ARDEC directed ATK under contract DAAE30-01-9-0800 TOSA 59/88 to process three web sizes, the target of 0.61 mm (0.024"), a smaller web 0.51 mm (0.020") and a larger web 0.70 mm (0.0275"). The web target changes the specific surface area for the propellant. A larger web reduces the surface area per unit mass and, subsequently, slows down the release of propellant chemical energy.

2.3 Processing Information

The PAP-8386 was processed by ATK under contract DAAE30-01-9-0800 TOSA 59/88 at the Radford Army Ammunition Plant in Radford, Virginia on the solventless manufacturing line. The solventless process includes: paste production, pre-roll, evenspeed, cob makeup, extrusion, grain cutting, annealing, deterrent coating, annealing, graphite glazing, and packaging. The process is pictorially shown in Figure 1.

In the solventless process, nitrocellulose is mixed with nitrate esters such as nitroglycerine or DEGDN in a water intensive slurry mixing process. The majority of the water is removed from the material in centrifugal wringer to create a wet paste very similar in appearance to artificial snow. The paste is weighed out into plastic totes that are metal detected and queued up in a magazine.

The paste is blended with any additional chemicals in a large cement mixer style blender barrel before it is weighed out and fed into the 'prerolls'. The preroll operation consists of two large heated metal rollers moving at different speeds. The paste adheres to one roll and the material is worked by a squeezing action between the two rolls. Much of the remaining moisture is removed by this process. The output from the rolls is a 'preroll' sheet.

Several preroll sheets are combined to make up an evenspeed pad. This pad is fed into the evenspeed equipment. The evenspeed equipment is simply two large heated metal rollers. The propellant sheets are fed between the rollers and the final mixing is accomplished by the squeezing action of the material in the roll bite.

Once the material has been fed through the rolls a number of times, it is rolled up and cut to form carpet roll 'cobs' that can be loaded into a cylindrical extrusion press basket. For this study, a 4-inch horizontal solventless press was used to extrude the material into the desired configurations. The extruded material was cut to length on a small-arms cutting machine.

Following manufacture, the propellant grain was characterized both chemically and physically. The results are shown in Table 4 (Physical dimensions). The process was capable of matching the target levels for the formulation and physical dimensions within a reasonable tolerance. Absolute density measurements were made and at 1.60 g/cc fell within the typical double base propellant range.

Table 4. Physical dimensions for PAP8386 candidates

Dimension	Blue 0.70 mm	Yellow 0.61 mm	Red 0.51 mm
Length, [mm]	1.88	1.92	1.90
Outer Diameter, [mm]	1.97	1.98	1.96
Web, [mm]	0.68	0.62	0.49
Inner Diameter, [mm]	0.62	0.74	0.99

2.4 Closed Bomb Characterization

The best way to assess propellant performance is through combustion testing. The closed bomb test is a standard device used to measure gasification rates for energetic materials. Knowledge of propellant chemical formulation and geometry allows for calculation of a linear burn rate from the measured pressure versus time data.

Even more conveniently, the closed bomb can be used to directly measure the relative performance of two propellants (MIL-STD-286C, Section 801.1). Table 5 shows the closed bomb comparison between the PAP8386 candidates and standard 25mm M793 propellant (RP-36)

at various temperatures. Performance is given in terms of relative quickness (RQ) and relative force (RF). Relative quickness applies to the speed with which the material burns and is a comparison of the pressurization rates (dP/dt). Relative force is a comparison of the peak pressure levels observed in the bomb (Pmax). Numbers are presented as a percentage of the candidate material (PAP8386) relative to the standard material (RP36).

Table 5. Relative performance of PAP8386 candidates to RP36

	Blue 0.70 mm	Yellow 0.61 mm	Red 0.51 mm
RQ @ 21 C	68	78	93
RF @ 21 C	104	104	104
RQ @ 65 C	77	89	106
RF @ 65 C	105	106	106
RQ @ -54 C	58	66	78
RF @ -54 C	102	103	102

To provide a visual comparison of the relative performance, a variable called dynamic vivacity (Machalka, 1982) has been reviewed. This comparison is shown in Figures 1 through 3 for the three different candidates. In these plots, the dynamic vivacity has been calculated and plotted against the normalized pressure in the closed bomb (P/Pmax).

The dynamic vivacity is calculated at each time step. It is determined by the following equation:

$$\text{Vivacity} = [dP/dt] / (P*P_{max})$$

The plots clearly show the influence on the burn speed for the various candidates. Higher vivacity values are an indicator of higher gasification rates. Assuming burn rates are constant, the changes in the gasification are due to an increase in the burning surface area.

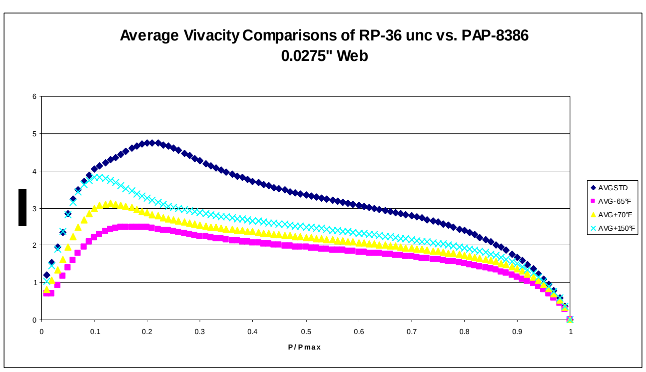

Figure 1. PAP-8386 vivacity results for the large web candidate (0.71 mm)

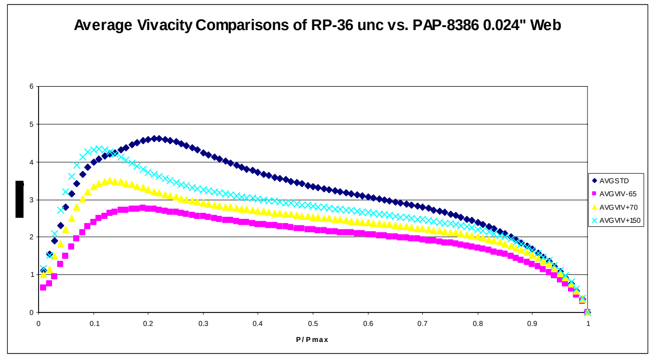

Figure 2. PAP-8386 Vivacity Results for the Target Web (0.024")

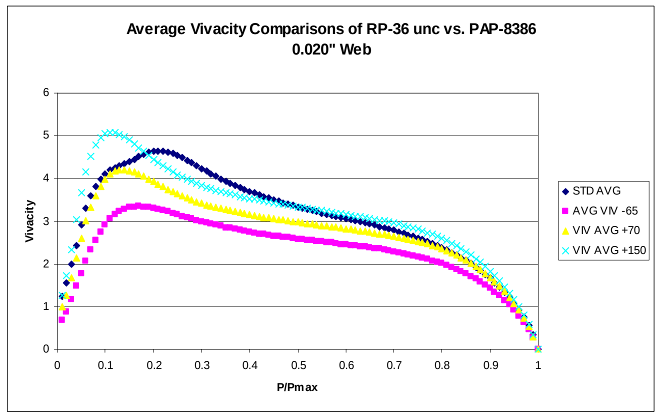

Figure 3. PAP-8386 Vivacity Results for the Smallest Web (0.020")

2.5 Deterrent Coating

To further improve the interior ballistic efficiency, ATK was directed by ARDEC under contract DAAE30-01-9-0800 TOSA 59/88 to apply deterrent coatings to the exposed propellant surfaces as part of the finishing process. This serves to reduce the propellant burn rate during the very early part of the ballistic cycle. As the projectile moves down bore, the burn rate increases as the outer layer burns away. By optimizing this coating process to match the movement of the projectile, the gasification rate can be increased as the volume behind the projectile increases.

Deterrent coating at Radford Army Ammunition Plant for this project was accomplished in small scale sweetie barrels using a proprietary system. A combination of penetrant and inhibitor deterrents was applied to the grains as part of a coating optimization investigation. Multiple deterrents were implemented based on previous work involving highly plasticized propellants.

Once again, the closed bomb was used to provide a comparative evaluation against standard 25mm M793 propellant (RP-36). This is shown using vivacity in Figure 4.

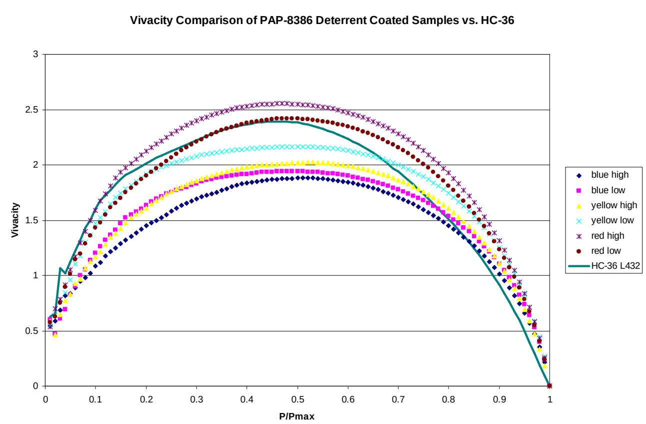

Figure 4. PAP-8386 Vivacity Results for Deterrent Coated Grains

Description of the nomenclature used in the legend for the figure is:

Blue high = 0.0275" web, high deterrent coating levels

Blue low = 0.0275" web, low deterrent coating levels

Yellow high = 0.024" web, high det. coating levels

Yellow low = 0.024" web, low deterrent coating levels

Red high = 0.020" web, high deterrent coating levels

Red low = 0.020" web, low deterrent coating levels

Throughout the remainder of this report, the nomenclature referring to web color will always be as referenced above.

3. BALLISTIC TEST RESULTS

The final proof of performance for any propellant system is gun testing in the final configuration. The initial ballistic results for the various web configurations are given in Table 6. These firings were carried out in the M793 cartridge using uncoated propellant grain PAP8386 at ambient conditions (21 °C). Charge weights were varied to determine optimal load conditions.

Table 6. Uncoated Propellant Gun Test Results of the PAP-8386

Sample	Chg Wt (g)	Velocity (m/s)	Pressure (Mpa)	AT (ms)
Bue Die - MFC-8	72	1029.2	381.6	3.024
Bue Die - MFC-5	75	1053.3	433	2.932
Bue Die - MFC-2	78	1095.3	461.9	2.805
Bue Die - MFC	80	1120.5	501.2	2.724
Yellow Die - MFC-8	67	1022.2	384.8	3.125
Yellow Die - MFC-5	70	1054.2	413.5	3.059
Yellow Die - MFC-2	73	1084.9	448.9	2.976
Yellow Die - MFC	75	1108.5	472.6	2.911
Red Die - MFC-8	59	991.8	354.9	3.192
Red Die - MFC-5	62	1020	374.2	3.093
Red Die - MFC-2	65	1048.4	417.8	3.086
Red Die - MFC	67	1066.6	448	3.104

Note: MFC = Max Full Case. i.e, MFC-8 = Max Full Case minus 8 grams of propellant.

The performance requirements for ambient conditions are a muzzle velocity of 1100 m/s and a mean pressure below 402 MPa. For all three dies, the pressure levels were too high indicating a need to slow the burning down early in the ballistic cycle. Because of limited quantities of Yellow Web propellant samples, only the Blue Web (0.71 mm) was subjected to intermediate ballistics testing. These results were used to help guide the final ballistic test configuration for the Yellow Web material. Based on the closed bomb tests results, the Red Web was determined as a fast burning propellant and did not follow the expected form function. As a result, it was not selected as a propellant candidate .

To slow the initial pressurization rate down early in the ballistic cycle, deterrents were applied to the blue web propellant. After the deterrent coating process was completed, additional ballistic tests were conducted. A blend of uncoated and coated propellants was shot in an effort to meet the ballistic targets. Once again, all testing was carried out at ambient temperatures (21 C) in the M793 cartridge. The results for each blend scheme are shown in Table 7. The blend scheme consisted of a combination of 50/50, 70/30, and 20/80 ratio of the coated and uncoated propellant grains.

Table 7. Firing results of a blend of coated and uncoated PAP-8386.

Sample	Chg Wt (g)	Velocity(m/s)	Pressure (MPa)	AT (ms)
Low Deterrent Coat				
Blue Die 50/50	75	903	237	6.2
Blue Die 50/50	78	921	254	5.5
Blue Die 50/50	80	934	261	5.5
Blue Die 70/30	75	868	218	7.1
Blue Die 70/30	78	895	233	6.5
Blue Die 70/30	80	907	245	5.8
Blue Die 70/30	82	932	258	5.7
High Deterrent Coat				
Blue Die 30/70	75	937	272	4.5
Blue Die 30/70	78	980	310	4.0
Blue Die 30/70	80	1010	339	4.1
Blue Die 20/80	75	958	289	4.1
Blue Die 20/80	78	1004	327	4.0
Blue Die 20/80	80	1022	347	4.0

Note: Coated Reference Refers to coated/uncoated percentages

From the intermediate tests, a final blend configuration was chosen for a final set of ballistic tests. The Blue Web (0.70 mm) final propellant blend was an 80% uncoated, 20% coated blend. The Yellow Web (0.61 mm) was a 70% uncoated, 30% coated blend. Final ballistic results are shown in Tables 8 and 9.

Table 8. Ballistic Results of PAP8386 Blue Web (0.70mm) at 21 C

Round #	Charge Weight [g]	Muzzle Velocity [m/s]	Pressure [MPa]	Action Time [msec]
1	85.5	1070	389.5	3.365
2	85.5	1090	409.2	3.364
3	85.5	1082	389.4	3.422
Average	**85.5**	**1081**	**396**	**3.384**

Table 9. Ballistic Results of PAP8386 Yellow Web (0.61 mm) at 21 C

Round #	Charge Weight [g]	Muzzle Velocity [m/s]	Pressure [MPa]	Action Time [msec]
1	83.0	1079	404.7	3.752
2	83.0	1085	395.9	3.799
3	83.0	1090	401.7	3.806
Average	**83.0**	**1085**	**400.73**	**3.786**

Additional ballistic testing was conducted at Picatinny across the operating temperature. It should be noted that this propellant geometry had increased ballistic pressure at cold. The increased pressure at cold was attributed to thin walled propellants and grain fracture under extreme cold conditions. Hot propellant performance was well within specification.

4. SENSITIVITY AND COMPRESSIVE MECHANICAL TESTING OF UNCOATED PROPELLANT

Although its applicability to system level IM performance is not firmly established, the PAP8386 behaved very well in the preliminary hazards sensitivity tests. These tests are standard measures of energetic materials initiation sensitivity to impact; friction and electrostatic discharge (see for example Headquarters, 1998). They are carried out primarily to assess the handling requirements of the propellant during the manufacturing process.

Most notably the PAP8386 had better small-scale impact properties than RPD-380 and JA2, two double base propellants currently fielded in tactical rounds by the U.S. Army. Both these propellants show very good response characteristics to shaped charge jet impact, bullet impact, and fragment impact tests in their fielded configurations. It is expected that PAP8386 will also show good response to mechanical stimuli based on these preliminary results.

In the friction test, the uncoated PAP-8386 propellant had very acceptable performance results with no reaction occurring for a ten sample series at 240 Newtons and reaction observed at 250 Newtons.

To further assess the uncoated PAP-8386 propellant potential IM response features, a high rate compressive mechanical test was carried out by ARL on the PAP8386 formulation. Due to the small propellant grain geometry, this sample could not fit into the sample tester anvil. As a result, this testing was carried out as part of a different study using the same propellant formulation but a larger propellant grain to fit into the sample tester anvil. For this sister project, larger seven-perforated grains were being studied. These grains were well-suited for testing in the ARL High Rate Material Test Systems Servo-Hydraulic Tester (Lieb and Rocchio, 1982).

Two lots of uncoated PAP8386 granular propellant were comparatively tested against a JA2 granular propellant for mechanical response at ambient pressure and temperatures of 21ºC, 63ºC, -32ºC, and -46ºC. The materials were tested in uniaxial compression to ~50 percent end strain using a deformation rate of 1.0 meters per second.

At 21º C, the uncoated PAP8386 and the JA2 showed good response to uniaxial compression. The failure modulus values measured for the uncoated PAP8386 lot at 21º C demonstrates the materials ability to sustain load and maintain mechanical integrity. The stress vs. strain plot, Figure 5, shows the PAP8386 and the JA2 lots work

hardening beyond failure, ~7 percent strain. The tested specimens, shown in Figure 6, for the PAP8386 lots at 21º C suffered permanent deformation and very minimal fracturing while the JA2 lot showed permanent deformation and barreling. (The lateral fracture observed in the specimens was tensile splitting that occurred at high strain due to barreling.)

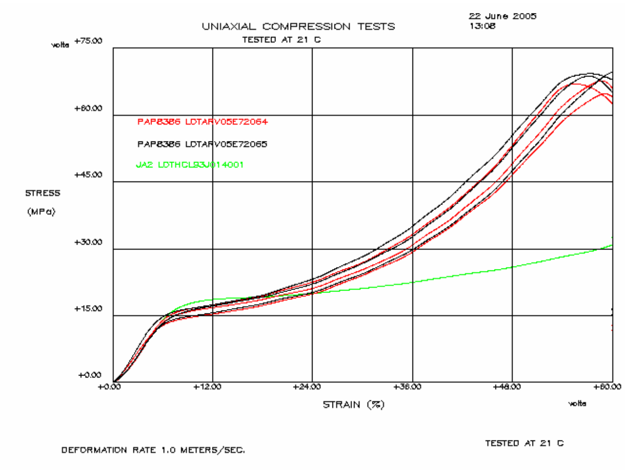

Figure 5. Stress vs. Strain of PAP8386 and JA2 at 21º C

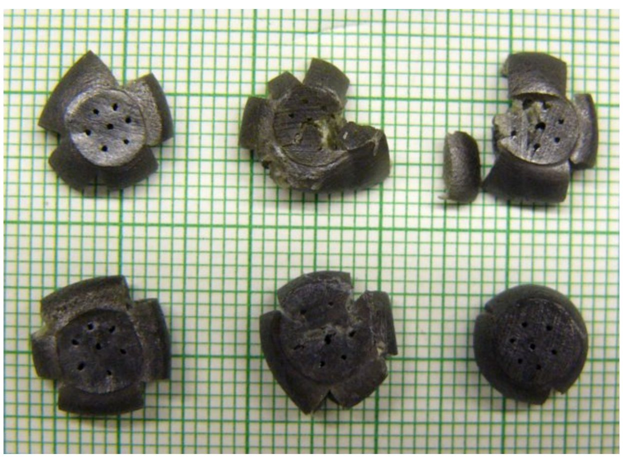

Figure 6. PAP8386 specimens from 21º C tests

At 63º C, again, the mechanical response of the PAP8386 and JA2 lots were quite good. The Young's compressive modulus values at 63º C indicated some "material-softening" when compared with the 21º C values. This result at higher temperatures is expected; however, extended exposure to temperatures at 63º C and above may cause agglomeration of these materials and quite possibly affect the ballistic performance. The stress/strain data shows the PAP8386 lot again, able to sustaining load and maintain mechanical integrity. The PAP8386 and JA2 lots continued to work harden after failure to ~50 percent strain. The PAP8386 tested specimens showed test damage in the form of permanent deformation and some barreling due to the softening observed at 63º C.

At -32º C, the stress/strain (Figure 7) plot clearly shows the PAP8386 lots to be a superior performer. The stress/strain plot and the failure modulus values indicate the ability to sustain loading to ~50 percent strain. The tested specimens (Figure 8) from lot PAP8386 suffered only minimal amounts of axial and shear fracture. The tested chards from the JA2 lot showed moderate amounts of axial and shear fracture.

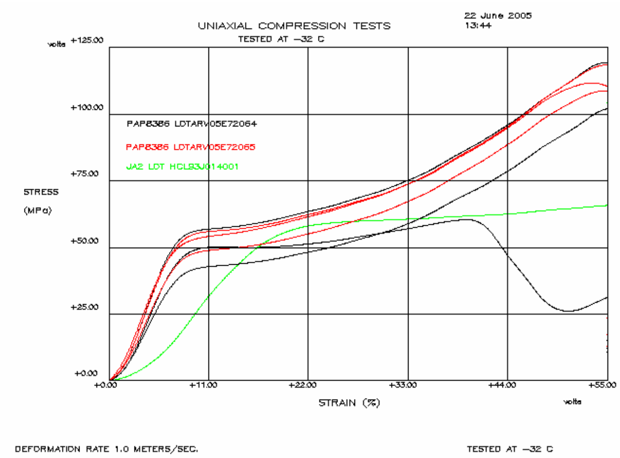

Figure 7. Stress vs. Strain of PAP8386 and JA2at -32º C

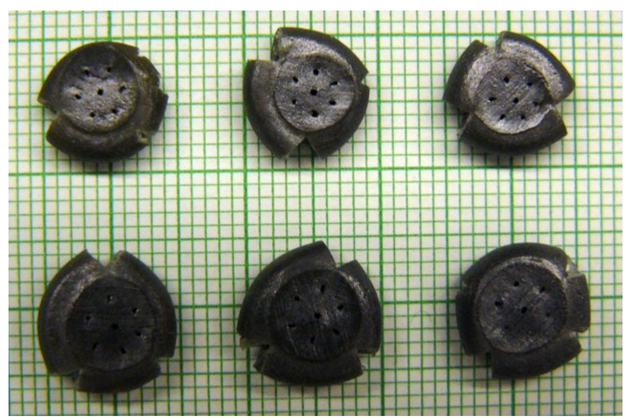

Figure 8. PAP8386 specimens from -32º C tests

At -46º C, again the PAP8386 lots showed excellent mechanical properties. The stress/strain plot and the failure modulus values achieved for lot PAP8386 indicated these materials able to sustain load to ~50 percent strain. The tested specimens from lot PAP8386 suffered only minimal amounts of axial and shear fracture.

Overall, the PAP8386 mechanical response was very good. In particular, the -32ºC and -46ºC responses were

most impressive. The minimal amount of fracture observed at these temperatures is atypical of the single-, double-, triple-base, and composite gun propellants that have been mechanically tested by the Army Research Laboratory.

5. CONCLUSIONS

A new double base propellant, PAP-8386, manufactured using a solventless process shows great promise as a propellant for medium caliber applications such as the M793. The solventless process eliminates the use of VOC's during manufacture and allows for a formulation that does not contain several environmentally hazardous ingredients.

Small-scale mechanical testing indicates superior response features relative to JA2, one of the most effective propellants in the Army's inventory. IM response of this propellant to impact stimuli is expected to be very good.

Acceptable ballistic performance in the M793 round was observed at ambient and hot temperature conditions. Due to the limitations of the extrusion hardware, there were some problems meeting cold temperature requirements. Additional work will be needed to improve cold temperature delta pressure performance. During ballistic firing, gunners commented that no odors were noticeable during the firing sequence.

6. FUTURE WORK

Additional work has been funded by ARDEC to investigate optimized physical characteristics of the propellant. New tooling will be fabricated to improve the structural integrity of the granulation. This should minimize the cold breakup problems experienced during the ballistic testing. In addition, a seven perforated propellant configuration will be investigated for potential LW30 applications.

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